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ESTIMATION OF PLATINUM, GOLD AND SILVER IN ALLOYS.

By Percy A. E. Richards, F.I.C.,

(*Read at the Meeting, June* 4, 1902.)

The need for a simple and satisfactory method for the estimation of the percentage of platinum in samples of platinum alloy has long been experienced by dental metallurgists. Various processes have from time to time been suggested, but most of these entail considerable difficulty in obtaining accurate results.

The following experiments were carried out to discover, if possible, a process that should be at the same time both speedy and accurate.

(*a*) Alloys containing Platinum and Silver only.

In the first place, a weighed quantity of the alloy was boiled with aqua regia in a small flask until action ceased, but the result obtained was far from satisfactory, as the formation of the silver chloride retarded, and finally stopped, the action before it was nearly completed.

Another piece of alloy of known weight was then boiled with strong nitric acid in a flask until action ceased, and the addition of more acid produced no effect. The contents of the flask were diluted with water and the platinum filtered off and washed. It was at once evident, however, that a certain portion of the platinum had dissolved with the silver, whilst further examination showed that some of the silver had been retained in the mass of the platinum.

An endeavour to meet this difficulty was made by fusing a weighed portion of the alloy with two and a half times its weight of silver, the button so obtained being beaten out, rolled into a cornet, and boiled with nitric acid as before. Under these conditions, it has been stated, the whole of the platinum will dissolve with the silver. This, however, does not appear to be the case, as it was found that only a small percentage of the platinum dissolved, the greater portion remaining as a black powder. This process was repeated, using larger proportions of silver in the initial fusion, viz., four and six times the weight of the original alloy, but in each case the

bulk of the platinum remained insoluble, although a considerable portion had dissolved. This necessitated the separation of the soluble platinum from the silver, and to effect this the filtrate and washings were heated to boiling, a little strong hydrochloric acid added gradually until precipitation ceased. The silver chloride was filtered off, well washed with water, dried and weighed. The filtrate from the silver was evaporated just to dryness, a few drops of water added, and the platinum precipitated with ammonium chloride in the presence of alcohol. The platinum was obtained from this by heating in a crucible in the ordinary way, its weight being added to that of the major portion yielded in the first stage. The fact that the platinum is only partially soluble under these conditions militates against the success of the estimation, and there is also the possibility of loss during the gentle heating of the bulk of the metal for the purpose of drying it. The experiments showed that after the nitric acid treatment the metal was rendered sufficiently explosive to frequently eject the contents from the crucible during the drying process.

These objections sufficed to condemn the method, and strong sulphuric acid was next used in place of nitric acid.

As before, a small piece of the alloy (about 0·3 gramme) was weighed, placed in a parting flask, about 10 c.c. of strong pure sulphuric acid added, and the flask heated for about fifteen minutes over a Bunsen burner until action had apparently ceased for quite a couple of minutes. The acid was allowed to thoroughly cool, and was then poured off the platinum into a beaker containing distilled water, the metal being again treated with strong sulphuric acid (about 5 c.c. were found sufficient). The flask and contents were again heated for five or ten minutes, and the acid poured off and added to the first quantity; owing to the great density of platinum this was effected without any difficulty. The metal was washed twice with water, the washings being added to the silver sulphate solution, and next with several quantities of water to free it from acid.

The platinum was then transferred to a crucible by filling the flask completely full of water and inverting over the latter, in which there was also a little water, the metal thereby falling into the crucible without loss. The greater part of the water was decanted off, and the metal dried in the air-bath before weighing.

The results obtained by this process were very satisfactory, as shown in the following table:

Alloy taken.		Platinum found.		Platinum per Cent.
0·384 gramme	...	0·128 gramme	...	33·5
0·432 ,,	...	0·144 ,,	...	33·4
0·357 ,,	...	0·119 ,,	...	33·4
0·395 ,,	...	0·139 ,,	...	33·5

The platinum residue was tested for silver, but was found to contain a minute trace only. The platinum at the end of the experiment was not disintegrated to powder as one should expect, but retained more or less its original shape, presenting, however, a decidedly blistered appearance. The drying was effected without any of the explosive phenomena observed in the nitric acid process.

The silver may be estimated in the acid filtrate, if desired, by the well-known sulphocyanide method, or, in the case of dental alloy, taken by difference. The metal

can also be recovered in the following simple way: The diluted silver sulphate solution, rendered slightly alkaline with ammonia, is warmed with a little glucose solution, and the precipitated silver filtered, washed, and dried.

(*b*) Alloys containing Gold, Platinum, and Silver.

For the purposes of experiment, various alloys were prepared containing a known percentage of gold, platinum, and silver. Each ingot was filed, and weighed portions of the filings used for analysis, the weights taken varying from 0·3 gramme to 0·6 gramme.

The first process employed consisted in heating the alloy to a moderate temperature in an atmosphere of chlorine under various conditions, but the results obtained were not always accurate, as the silver chloride formed was apt to fuse and prevent complete chlorination taking place.

The alloy was next treated with boiling sulphuric acid as described previously, and this method proved much more satisfactory. After the acid extraction the residual gold and platinum was washed, dried, and weighed as a check on the figures obtained. The residue was then dissolved in nitro-hydrochloric acid, concentrated to a small bulk, and the platinum precipitated as ammonia-platinum chloride, the latter strongly heated and the metal weighed.

The gold in the filtrate from the ammonia-platinum chloride was thrown down by ferrous sulphate, washed, dried, and weighed. For the reasons given above, treatment of the original alloy with aqua regia was found to be quite unsuitable.

The following results were obtained from the analysis of one of the alloys:

	Platinum.	Gold.	Silver.
No. 1	5·65	26·62	67·84
,, 2	5·51	26·47	67·92
,, 3	5·26	26·73	67·81

(*c*) Alloys containing Gold, Platinum, Silver, and Tin.

The method of analysis that gave the best results in this case was practically identical with that last described.

A weighed portion of the alloy filings was extracted with boiling sulphuric acid several times as before, silver and tin being dissolved, whilst platinum and gold remained behind. The residue, well washed and dried, was weighed, the platinum and gold being afterwards separated and estimated as before. The silver was determined by titrating the sulphuric acid solution, and the tin calculated by difference.

Analysis of an alloy examined in this way gave the following figures:

	Platinum.	Gold.	Silver.	Tin.
No. 1	2·20	9·30	58·52	29·98
,, 2	2·29	9·18	58·36	30·17

Attempts to use aqua regia to dissolve the alloy resulted in the formation of purple of Cassius with the silver chloride, and this effectually prevented a satisfactory estimation.

Heating the alloy in a tube through which a stream of chlorine was passed gave fair results, the tin chloride in this method being volatilized and estimated by difference, as attempts to collect it in water, with a view to precipitation, were not very successful.

The sulphuric acid process does away with the necessity for using chlorine, and this is a distinct advantage, whilst the results obtained are certainly better.

Discussion.

Mr. Allen said that many years ago he had had occasion to examine alloys of a somewhat similar character to those mentioned by the author, and he had then found nitric acid did not dissolve the whole of the platinum from a platinum alloy, although the contrary had been stated to be the case. One particular dental alloy of tin and gold, on treatment with nitric acid, left a residue of a purple colour, consisting either of purple of Cassius or a mixture of SnO_2 and finely-divided gold. On subsequent treatment with strong sulphuric acid this dissolved, leaving metallic gold, and yielding a solution of stannic sulphate. Stannic sulphate was analogous to, though less stable than, titanic sulphate. It could be kept indefinitely in solution in strong sulphuric acid, but if the solution were diluted with water, it gradually decomposed, even at the ordinary temperature, while on boiling it decomposed immediately into metastannic acid and sulphuric acid. That afforded a possible means of analysis, which he had found valuable at the time.

ON THE ACTION OF BOILING HYDROCHLORIC ACID UPON ARSENIC ACID.

By Otto Hehner.

(*Read at the Meeting, June* 4, 1902.)

In 1862 R. Fresenius published under the above title, in the first volume of the *Zeitschrift fuer Analytische Chemie*, p. 447, a paper in which he showed that, on boiling sodium arsenate, "free from every trace of arsenious acid," with strong hydrochloric acid, small but distinct quantities of arsenic were volatilized, the distillates giving, with hydrogen sulphide, slight yellow precipitates of the sulphide. With hydrochloric acid diluted with twice its bulk of water no arsenic could be detected by hydrogen sulphide in the first portions of the distillate, while the last portions gave evidences of volatilized arsenic.

This statement is referred to in Watts' Dictionary, first supplement, p. 222, published in 1879, and has generally gone into the literature on the subject. Thus Fresenius himself, in his "Quantitative Analysis," fifth edition, warns against evaporating arsenic solutions with hydrochloric acid unless care be taken often to replace the evaporating water to keep the acid from concentrating beyond a certain point. Otto, in his "Ausmittelung der Gifte," 1875, states that it is well known that on distilling strong hydrochloric acid containing arsenic acid much arsenic is volatilized as chloride. As recently as this year the statement is made (Erdmann, "Inorganic

Chemistry" [German], p. 368), "Concentrated hydrochloric acid partly reduces arsenic acid on heating"; and on p. 373, "Arsenic acid is but incompletely converted into arsenic trichloride" (on treating with NaCl and H_2SO_4).

In view of these statements it seemed improbable, to say the least, that hydrochloric acid could be readily obtained free from arsenic by adding an oxidizing agent, like permanganate or bichromate, and distilling, as stated in the recent discussion on this subject.

To satisfy myself I prepared some arsenic acid, perfectly free from arsenious acid, by evaporating 3 grammes of arsenic trioxide four times with strong nitric acid. The product, freed by evaporation on the water-bath from all but traces of nitric acid, was dissolved in 100 c.c. of water; 10 c.c., corresponding to 0·3 gramme of arsenic oxide, were distilled with 100 c.c. of pure, strong hydrochloric acid. The distillate was collected in fractions, and these were tested with hydrogen sulphide; all gave strong yellow colorations, a precipitate of arsenic sulphide gradually separating. A similar result was obtained when potassium permanganate had been added before the beginning of the distillation—in other words, when the distillation was commenced in the presence of free chlorine.

This result appeared fully to corroborate the previous knowledge of the subject, and it seemed probable that hydrochloric acid might be able to reduce other mineral substances, for it is a long-known fact that some organic substances, like quinones, are reducible by hydrochloric acid.

On boiling a solution of ferric chloride (free from ferrous salt) with hydrochloric acid, both without and with the addition of permanganate, the residue in the distilling-flask showed a strong reaction for ferrous iron by means of potassium ferricyanide.

In order to prevent, in the above experiment, any mechanical carrying over of arsenic from the distillation-flask, I had fitted to it a long fractionation-tube by means of a cork. As, however, it seemed possible that the organic matter of the cork might have played a part in the reducing actions observed, I repeated the experiments with a similar apparatus having nothing but ground-glass connections. Under these conditions no formations of ferrous salts could be observed from ferric chloride, ferricyanide giving no trace of a blue coloration. In the case of arsenic acid the distillates showed no trace of any discoloration with hydrogen sulphide. This was the test solely relied upon by Fresenius, upon whose authority the statements in the books are founded. He used in his experiments a tubulated retort, with its neck turned upwards, but he does not say whether the tubulus or the retort was closed with a cork or a glass stopper. In 1862 stoppered retorts were not so usual as they are now, and, from the internal evidence, I would say that a cork closure had been employed. It seems clear from his paper that he had no suspicion that organic matter might play an important part in the reaction, for he states that, when organic substances have been "destroyed" by hydrochloric acid and chlorate, no fear of volatilization of arsenic need be entertained, provided that the said acid be kept sufficiently diluted.

The whole of the distillates, which failed to show arsenic by hydrogen sulphide, gave, however, plain indications of the presence of traces of arsenic by the Marsh-

Berzelius method. No fraction could be obtained that was satisfactorily free from arsenic. Nevertheless, the remarkable diminution in the amount of arsenic volatilized when the flask was connected with the fractionation-tube by glass only, as compared with cork connection, shows clearly that the reduction has been mainly, if not entirely, brought about by the presence of organic matter. The traces of volatilized arsenic observed even when the most scrupulous care had been taken to exclude organic matter, all parts of the apparatus having been thoroughly treated with strong sulphuric acid and potassium bichromate, are almost certainly due to the reducing action of organic dust. We have to deal in the case of the Marsh-Berzelius indication with small fractions of hundredths of milligrammes, and the dust in the air of the laboratory would be sufficient to account for the reduction.

In the well-known method of Fyfe and Schneider for the separation of arsenic from organic substances, depending upon the volatilization of the arsenic by boiling hydrochloric acid, no reducing agent was originally added, yet the arsenic present in the higher form of oxidation slowly distilled off. The organic matter itself served as reducing agent until Emil Fischer introduced the employment of ferrous chloride for that purpose.

Although I have not succeeded in obtaining from arsenic solutions a distillate absolutely free from arsenic—and it is almost impossible to devise any arrangement whereby every trace of organic matter, in the form of atmospheric dust, could be excluded in all stages of the operation—I believe I am justified in concluding that hydrochloric acid does not possess any reducing action *per se* upon arsenic compounds. Nevertheless, it is quite evident that it is not in practice a recommendable method to obtain arsenic-free hydrochloric acid, for the purpose of the Marsh-Berzelius test, from arsenical acid to which an oxidizing agent has been added. With reasonable care to exclude organic matter, only a minute fraction of the arsenic passes into the distillate. Thus Fresenius obtained from 10 grammes of sodium arsenate 4·4 milligrammes of sulphide, and I a much less but not determined quantity, from the arsenic acid produced 0·3 gramme arsenious acid. Hence, starting with a reasonably pure hydrochloric acid, it may be possible—and, after Mr. Allen's statement, we must take it that it *is* possible—to obtain in this way a distillate which fulfils the requirements of the method laid down by the Arsenic Committee; but my experiments clearly convince me that it is best to add a powerful reducing agent to drive off any arsenic there may be present, and to collect the distillate after such removal of the arsenic.

Discussion.

Mr. Allen observed that Mr. Hehner's experiments showed strongly the necessity for the greatest care when these infinitesimal quantities of arsenic were being dealt with. Many conditions which were apt to be ignored and considered unimportant really played an important part in affecting the results. For himself, he could simply say that he had found, even in the case of hydrochloric acid containing considerable traces of arsenic, that the addition of a moderate excess of potassium permanganate and subsequent distillation yielded acid which, by the Marsh-Berzelius test, gave no indication of the presence of arsenic. But, after the experiences recorded by

Mr. Hehner, he would be quite prepared to find that, unless the conditions of success were discovered and rigidly adhered to, that method might break down as others had done.

Mr. E. H. Jeffers said that, in the method of purification proposed by Dr. Thorne and himself—which was really a modification of the Reinsch process—one of the ordinary old-fashioned retorts was used, inclined upwards, the distillate being collected in a Wurtz flask placed with the side tube downwards, hence there were no organic connections. After the apparatus had been working for a few minutes the atmosphere inside the retort became practically free from organic matter. The specific gravity of the acid was, roughly, 1·100 to start with, and it practically continued to distil over at that gravity. The acid was supplied from a reservoir through a tube which passed down to the bottom of the retort, and round the lowest extremity of this tube a piece of copper gauze was placed. When once the solution was obtained colourless there was no further difficulty, the distillate being perfectly free from arsenic. The reducing action of the hydrochloric acid was shown by the fact that the acid previously extracted with copper gauze gave a dark-green solution on cooling overnight, whilst on heating the solution in the morning without copper its colour lightened considerably, and this must be due to the fact that the cupric chloride formed had already become partially reduced. It seemed to be of importance that the specific gravity of the acid should not vary from about 1·100.

Mr. Hehner said that, if the arsenic was simply removed by distillation, he did not quite understand what bearing that would have upon his observations with regard to reduction, as the arsenic, after being boiled with the copper, would be already in the arsenious condition.

Mr. Allen said that since, after distillation, traces of arsenic were left behind in the acid, in presence of cuprous chloride it would be expected that such traces of arsenic, being in the arsenious state, would also come over on continued distillation.

Mr. Jeffers said that the function of the copper was simply to keep the solution absolutely reduced. As soon as the solution boiled, the copper and the cupric chloride formed on cooling reacted, the dark-green solution becoming perfectly colourless. As the solution entered the retort it was reduced, and distillation was carried on so long as the liquid in the retort remained colourless. So long as the specific gravity of the solution did not exceed 1·100 no arsenic distilled over. If, however, the solution was thoroughly reduced to begin with, the copper would be blackened, owing to erosion and solution of the copper in the cupric chloride solution, and not to the deposition of arsenic.

THE USE OF BORIC ACID AND ITS SALTS AS FOOD PRESERVATIVES.

The following series of articles are freely translated from abstracts appearing in the *Zeit. für Untersuch. der Nahr. und Genussmittel*, 1902, v., 678-682 :

On the Action of Boric Acid and Borax on Human Beings and Animals. E. Rost. (*Arb. Kaiserl. Gesundh.-Amt.*, 1902, xix., 1-69.)—As the antiseptic action of boric acid is small, comparatively large quantities are necessary to preserve

articles of food, it is quite possible for a person to take as much as 3 grammes daily of the preservative in his ordinary food. Meats, sausages, milk, butter, margarine, white and yolk of egg, fish, caviare, shellfish, etc., are frequently preserved by the addition of boric acid. The author found 3·87 per cent. in dry salt meat and 2·8 per cent. in shrimps. Boron compounds are stated to have no specific action on the enzymes of the stomach and intestines, except as regards their acid or alkaline properties. Borax retards to a small extent the coagulation of milk by rennet; the addition of borax to milk, especially when the latter is intended for infants' food, is therefore injurious. Large doses were found to cause local irritation and inflammation in dogs, cats, and rabbits, and also affected the action of the bowels. In two experiments on men it was found that doses of 1, 2, and 3 grammes of boric acid retarded the assimilation of albuminoids, the nitrogen contents of their urine being determined hourly before and after taking the boric acid. By taking the temperature of various dogs fed on borated meat, it was demonstrated that assimilation of the food was delayed. Experiments on other dogs showed that only large doses caused a loss of corpuscular albuminoids. It may be here mentioned that no essential difference was noticed in the action of boric acid and borax. A striking loss of weight of the animals was noticed. As this was not due to destruction of albumin or loss of water, it must be put down to oxidation of fat. Apparent increase in the digestion of albumin, shown when very large doses of borax were given, was due to the "salt" action of the borax, similar results being exhibited by large doses of common salt and potassium nitrate. A large consumption of water prevented these effects.

Assimilation experiments in the presence of boric acid were also carried out on four assistants. During a preliminary period of five to seventeen days the men were brought into a state of "nitrogen equilibrium," followed by administration of boric acid (3 grammes per diem) for twelve days. Two of the men then for a time received no boric acid, and afterwards underwent a second treatment. Finally, some days were devoted to studying the after-symptoms of the experiments. Two of the men showed a loss of weight due to loss of fat. The final observations also showed less secretion of urine and absorption of nitrogenous food materials. The two other assistants also showed a loss of weight. These two latter were also chosen for Rubner's experiments (see next paragraph), in which the amounts of expired carbon dioxide and water were determined. One of them diminished so suddenly in weight after taking 3 grammes of boric acid daily that the experiment had to be discontinued. The weight of the other also decreased, but increased when the boric acid was discontinued, and again fell when the latter was readministered. It was not demonstrated by the above experiments that boric acid affected the appetite. No influence upon health and appetite was noticeable.

Boric acid was not found by the author to influence the temperature, blood-pressure, or kidneys. As the elimination of boric acid by the urine takes from eight to fourteen days, its action is probably cumulative.

The author comes to the conclusion that the use of boron compounds in food should be forbidden.

The Action of Boric Acid on the Digestion. Rubner. (*Arb. Kaiserl.*

Gesundh.-Amt., 1902, xix., 70-88.)—According to the author, who comes to the conclusion after numerous experiments, boric acid has an important latent action on the digestive process. Not only the digestive organs themselves, but the whole alimentation is affected. The change produced, which may amount to a loss of 22 per cent. of energy and 30 per cent. of the utilization of nitrogen-free food, is a very important fact, and undoubtedly means injury to health, as the amount of fat in the body may be of the greatest importance, and the reduction of the fat must be followed by a rapid fall in albuminoids. Serious results may result in infant feeding, to invalids, old people, or convalescents by borated foods.

The Influence of Borax on Metabolism in Man. R. O. Neumann. (*Arb. Kaiserl. Gesundh.-Amt.*, 1902, xix., 89-96.)—The experiments carried out by the writer on himself consisted of a preliminary period of four days, during which various observations were taken; then ten days with daily doses of 3 grammes of borax, followed by four days without borax, and concluding with daily doses of 5 grammes of borax for three days. During the first period nitrogen equilibrium existed; the secretion of nitrogen decreased during the first borax treatment, also in the intermediate four days, but was not further diminished by the larger doses of borax. His weight fell 1,200 grammes in seven days of the borax period. The flow of urine was somewhat increased, and boric acid could be detected for eighteen days after the last dose of borax had been taken.

The Influence of Boric Acid on the Utilization of Food. A. Heffter. (*Arb. Kaiserl. Gesundh.-Amt.*, 1902, xix., 97-109.)—Four series of experiments were made, a considerable time apart. In each the author first fasted for eighteen to twenty hours, and then lived on milk (2 to 3 litres) and eggs (10) for forty-eight hours, afterwards again fasting for eighteen to twenty hours. In two of these periods no borax was taken, and in the other two the food was borated, one by taking 1 gramme of boric acid daily and in the second 4 grammes daily. In all the experimental periods the total nitrogen and dry solids were estimated in the fæces, as well as in the milk, and calculated in the case of the eggs. The boric acid was found to increase the solids and nitrogen in the excreta. When 1 gramme of boric acid was taken for two days, the dry solids amounted to 6·3 per cent. and the nitrogen 5·09 per cent. of the amount taken. By taking 4 grammes of boric acid in two days, the amounts were 8·8 per cent. and 8·9 per cent. respectively. During the time when no boric acid was taken the dry solids were 3·6 and 4·5 per cent., and the nitrogen 3·0 and 3·9 per cent. for the two days. The increase of the nitrogenous matter in the excreta was probably due to the diminished absorption of albuminoids as a result of the injurious effect of the boric acid on the mucous membrane of the intestines, boric acid often causing diarrhœa. The conclusion is that boric acid is not without objection when used as a preservative.

Quantitative Estimations of the Excretion of Boric Acid from the Body. G. Sontag. (*Arb. Kaiserl. Gesundh.-Amt.*, 1902, xix., 110-125.)—Single doses of 3 grammes of boric acid were administered to three healthy persons, and the boric acid then determined in the urine by titration in the presence of mannite after the urine had been freed from phosphates and neutralized. The accuracy of this method was tested by preliminary experiments. It was found that the urine was only free

from boric acid after five, eight, and nine days had elapsed since taking the dose. About 50 per cent. of the boric acid was excreted in the first twelve hours, but the remainder very slowly. After the fifth day the quantity was so small that it could not be quantitively estimated. In all three experiments very similar results were obtained. It may be mentioned that in one case hourly variations were noticed, which were probably due to differences in the quantity of water secreted.

The Action of Rennet on Milk in the Presence of Boron Compounds and other Chemicals. A. Weitzel. (*Arb. Kaiserl. Gesundh.-Amt.*, 1902, xix., 126-166.)—Systematic experiments were made regarding the influence of ordinary preservatives and other compounds on the coagulation of milk by rennet. Aqueous solutions of the preservatives were employed when possible, but in the case of insoluble compounds the fine powder was added to the mixture of milk and rennet. Observations were taken as to whether the action of the rennet was accelerated or retarded by the chemicals used. The substances experimented with were divided into seven groups: (1) Alkaline: borax, sodium hydroxide, sodium carbonate, and sodium hydrogen carbonate. (2) Salts capable of precipitating lime: sodium oxalate, sodium fluoride, and sodium oleate. (3) Other salts having an alkaline reaction: sodium sulphite, salicylate, benzoate, propionate, acetate, and formate. (4) Neutral salts: sodium chloride, lithium chloride, sodium nitrate, perchlorate, tartrate, sulphate, ammonium sulphate, and magnesium sulphate. (5) Acid salts: sodium hydrogen tartrate, sodium hydrogen sulphate, and sodium persulphate. (6) Acids: boric, carbon dioxide, oxalic, benzoic, salicylic, protocatechuic, and gallic. (7) Formaldehyde, saccharin, and cane sugar.

The following results were obtained:

1. Borax retarded the coagulation when present in only small quantities (0·01 to 0·04 per cent.), and the amounts usually employed (1 gramme per litre of milk) stopped the action of the rennet altogether. All other alkaline salts acted similarly.

2. Coagulation was checked by those salts which precipitated the lime compounds. When the reaction became alkaline, the influence of alkalinity also showed itself.

3. The neutral salts generally had a retarding action. Some (sodium and lithium chloride) principally in concentrated solution, more feebly when present in small quantities. Magnesium sulphate in both concentrated and dilute solution had considerable influence.

4. Small quantities of the acids aided the coagulation. After carbon dioxide, boric acid had the most feeble action. The acid salts acted in the same manner as the acids.

5. The action of formaldehyde was so powerful that it must be considered as a direct poison to the rennet enzyme. Saccharin in small quantity had little influence, but stronger solutions greatly hindered the coagulation. Sugar, up to 20 per cent. of the weight of the milk, had no action.

The Amount of Boric Acid Present in Hams which have been Stored in Powdered Borax or Boric Acid. E. Polenske. (*Arb. Kaiserl. Gesundh.-Amt.*, 1902, xix., 167, 168.)—It is already known that fresh meat, when packed in borax, becomes thoroughly impregnated with the same. The author found the following quantities

of borax in a piece of unsmoked ham weighing 600 grammes, which had been embedded in powdered borax for three weeks: in the fat, 0·076 per cent.; in the centre lean part, 2·73 per cent.; and in the outside lean portion, 4·05 per cent. An experiment was then made to show that boric acid and borax will also penetrate smoked hams. Two smoked hams, each weighing 5·5 kilogrammes, were packed—one in powdered borax and the other in powdered boric acid—and kept for four weeks in a dry place at the ordinary temperature. The hams were then well rinsed with water, and a section cut from each measuring 10 centimetres long, 6 centimetres wide, and 6 centimetres thick. These sections were then cut, beginning at the outside end, into small pieces of 0·5, 0·5, 1, 2, and 2 centimetres. The borax in these pieces, proceeding from the outside inwards, was then found to be 0·449, 0·137, 0·0879, 0·0764, and 0·0955 per cent. in the case of the ham packed in borax. The other ham gave 0·273, 0·173, 0·099, 0·099, and 0·0244 per cent. of boric acid.

W. P. S.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOODS AND DRUGS ANALYSIS.

The Cholin Test for Cognac. H. Struve. (*Zeit. anal. Chem.*, 1902, xli., 284-289.)—The products sold under the name of cognac are: (1) genuine cognac distilled from wine and matured in oak casks; (2) sweetened cognac, in which the crude spirit, often obtained from inferior wines, is mixed with sugar and caramel before storing; and (3) a fictitious article prepared by mixing a crude spirit with various essences and fruit flavours. According to the author, cholin does not occur in wine, genuine cognac, or other alcoholic liquids prepared by the fermentation process; and he has come to the conclusion that cognac in which cholin is present must be regarded as belonging to the third class. For the detection of cholin 50 c.c. of the cognac, from which the alcohol has been distilled, are digested for a few moments in a porcelain dish with a few drops of dilute sulphuric acid, then mixed with an excess of slaked lime or lead oxide and evaporated to dryness. The residue is extracted with 97 per cent. alcohol, and the alcoholic extract, which is usually colourless, evaporated to dryness. The residue is dissolved in a few drops of water, and a little of the liquid evaporated on a microscopic slide at 100° C. As a rule, a non-crystalline white residue is left, though white crystals of lead chloride are to be observed when lead oxide was used in the first evaporation. A drop of iodine solution is then added, a cover-glass placed over it, and the slide examined under the microscope. In the presence of cholin the characteristic needle-shaped crystals of cholin iodide will be observed in a few moments. These crystals at first increase in size, and then disappear after a short time. When the preparation is completely dry they can be again produced by the addition of more of the iodine reagent.

C. A. M.

Detection of Coal-Tar Colours in Preserved Fruits (Jams), Marmalade, etc. Reichelmann and Leuscher. (*Zeit. für öffentl. Chemie*, 1902, viii., 205.)—A portion of the jam is diluted with water and boiled for one hour, after adding a few white woollen threads. The latter are then taken out, washed with cold water, and treated with about 20 c.c. of 2 per cent. ammonia, no notice being taken of any colour change. At the end of fifteen minutes the threads are withdrawn, the liquid is made acid with sulphuric acid, and fresh wool is added. If this wool be appreciably dyed and the colour be unaltered on treatment with ammonia, coal-tar dyes are present, and may be approximately identified in the usual way. The boiled aqueous solution of the jam may be tested for the presence of saccharin and salicylic acid.

W. P. S.

Detection of Coal-Tar Colours in Pastry, Cakes, etc. Reichelmann and Leuscher. (*Zeit. für öffentl. Chemie*, 1902, viii., 204, 205.)—The following method is given for testing pastry and cakes which have already been coloured to some extent by the eggs employed in making them. About 50 grammes of the ground material are boiled for one hour under a reflux condenser with 75 c.c. of acetone and 10 c.c. of water. The solution is then poured off into another flask, the acetone is distilled off, 30 c.c. of water are added to the residue, and, after cooling, the solidified fat is removed by filtration. A few white woollen threads are added to the filtrate, which is then warmed for half an hour. Should tar colours be present the wool is dyed, and the colour may be identified by the usual tests. Water must be added to the acetone in order to extract all the dyes, and the acetone must afterwards be removed as completely as possible, so that all the fat shall separate out from the solution. The colouring-matter of the eggs remains in the fat. W. P. S.

Detection of Red Sanders Wood in Cocoa. Reichelmann and Leuscher. (*Zeit. für öffentl. Chemie*, 1902, viii., 203, 204.)—Sanders (sandal) wood may be detected in cocoa-powders, to which it is sometimes added for the purpose of masking the addition of starch, by microscopical examination, or by the following colour tests. From 2 to 3 grammes of the sample are shaken with about 10 c.c. of absolute alcohol. With pure cocoa the alcohol remains colourless, or is coloured only a faint yellow; the solution gives a white precipitate with sodium hydroxide, and no reaction with ferric chloride. The filtered alcoholic extract from sanders wood, or cocoa mixed with the latter, is, on the other hand, coloured, and gives, with dilute sodium hydroxide solution, an intense violet coloration. Should the wood have been previously exhausted, this coloration is less pronounced. Ferric chloride also yields a deep violet colour with the extract from unexhausted wood, but in the case of exhausted wood this reaction is only to be obtained by allowing a drop of ferric chloride solution to run on to the surface of the alcoholic extract. A violet ring is then formed, which disappears on shaking. Acetone may be used in place of alcohol for making the extraction.

W. P. S.

Detection of Saccharin and Salicylic Acid in Foods. M. Spica. (*Gaz. chim. Ital.*, 1901, xxxi., [2], 41-46; through *Zeit. für Untersuch. der Nahr. und Genussmittel*, 1902, v., 620.)—The solution to be tested is shaken out with a mixture of ether and petroleum spirit, and the ethereal layer filtered through a dry filter. The filtrate is divided into three portions, which are placed in separate test-tubes and evaporated on the water-bath. The residue in one of the tubes is tested for salicylic acid by adding a few drops of concentrated nitric acid, warming the mixture, and dyeing wool with the resulting picric acid, if present. To another test-tube a little calcium oxide is added, and the tube heated until charring commences. The contents of the tube are then boiled with a few centimetres of water, and the solution is decanted into another tube containing a little hydrochloric acid and a small piece of zinc. After twenty minutes the solution is poured off, and a few drops of a solution of potassium nitrate and α-naphthylamine hydrochloride are added to it. Should saccharin have been present in the liquid under examination, a carmine red coloration is produced on standing for a few minutes. Extremely small traces of saccharin give a coloration after about an hour. The residue in the third test-tube is oxidized by the addition of a little sulphuric acid and potassium permanganate. After warming, any excess of permanganate is destroyed by means of oxalic or sulphurous acid, a little water is added, and a small quantity of a solution of diphenylamine hydrochloride is added to the bottom of the test-tube by a pipette. In the presence of saccharin a blue ring is formed at the junction of the two liquids.

W. P. S.

The Acetic Acid Test for Oil of Turpentine. P. W. Squire and C. M. Caines. (*Pharm. Journ.*, 1902, 512, 513.)—An acetic acid strictly complying with the British Pharmacopœia titration test (which requires the acid to be of 98·9 per cent. strength) does not form a clear solution with all samples of oil of turpentine when mixed in equal volumes. The acid must at least contain 99·5 per cent. of acetic acid to give clear solutions without subsequent turbidity. W. P. S.

Colour Reactions of Oil of Peppermint. P. Welmans. (*Pharm. Zeit.*, 1901, xlvi., 591, 592; through *Zeit. für Untersuch. der Nahr. und Genussmittel*, 1902, v., 633.)—P. Fiora has stated that oil of peppermint when mixed with phenol gives a greenish-blue coloration, which is destroyed by heating and reappears on cooling the mixture. Creosol, guaiacol, resorcinol, and sodium phenolate gave no reaction. The author finds that the reaction does not take place when absolutely pure phenol is used, but the addition of a drop of nitric acid free from chlorine causes the formation of a deep blue colour with a copper-coloured fluorescence. On warming, the colour changes to yellow. Chlorine, therefore, is not necessary to the reaction. The presence of acetic acid increases the intensity of the colour. Bromine and iodine give a violet coloration with the oil. The most pronounced blue colour is obtained by mixing 5 c.c. of oil of peppermint with 1 c.c. of iodine-mercuric chloride solution (25 grammes of iodine and 30 grammes of mercuric chloride dissolved in 1,000 c.c. of a mixture of acetic acid and acetic ether in equal parts). Mercuric chloride itself

dissolves to a considerable extent in oil of peppermint, giving a green colour on gently warming. Further heating first gives rise to a violet-blue or deep green colour, according to the amount of mercuric chloride present; the blue or green colour then disappears and the whole of the mercury is precipitated as subchloride. The supernatant liquid is yellow, becoming green on standing and finally blue. In the presence of much mercuric chloride a deep green colour remains throughout the heating. Prolonged boiling with silver nitrate causes a mirror to be formed.

W. P. S.

TOXICOLOGICAL ANALYSIS.

Notes on the Serum Test for Blood in Forensic Cases. Ogier and Herscher. (*Ann. de Chim. anal.*, 1902, vii., 241-245.)—The authors confirm the statement of Linossier and Lemoine (ANALYST, xxvii., 250) that serum rendered specific for human blood-serum may often give precipitates with solutions of the blood-serum of other animals; but they point out that, if the amount of precipitate and the rapidity with which it appears be taken into account, a definite conclusion can be arrived at. Thus, in solutions of human blood-serum at 38° to 40° C. a flocculent precipitate appears throughout the liquid after about ten minutes, and within about thirty minutes the precipitation is nearly complete, and there is an abundant deposit at the bottom of the tube. On the other hand, in the case of other blood sera the formation of the precipitate does not begin until after a much longer time, usually several hours, and is invariably smaller. In testing suspected blood-stains the authors treat the stain with distilled water and place the solution in small tubes 10 to 12 centimetres in length, by 4 to 5 millimetres in diameter. At the same time they prepare solutions of approximately the same strength of the sera of the blood of man, and of five or six domestic animals. A few drops of the prepared serum reagent are then added to each tube, and the whole of the tubes shaken and immersed in a water-bath at 37° to 40° C. If after thirty minutes no precipitate is formed in the tubes containing the solution under examination, the authors conclude that it does not contain human blood, and take no notice of any precipitate that may subsequently be formed. If, on the other hand, a positive result be obtained, they report that it is extremely probable that the stain consisted of human blood. As it is not possible to carry out control tests with the blood of an indefinite number of animals, a more positive assertion is, in their opinion, not justifiable. With negative results, however, the case is different. Thus, in a recent criminal trial the prisoner asserted that a recent blood-stain was caused by the blood of a rabbit. The authors therefore prepared a serum specific for rabbit's blood-serum, and when this gave no precipitate within thirty minutes with a solution of the stain they were able to state with certainty that the stain did not consist of rabbit's blood.

C. A. M.

ORGANIC ANALYSIS.

Reactions taking Place in the Determination of the Iodine Value. Harry Ingle. (*Journ. Soc. Chem. Ind.*, 1902, 587-595.)—As the result of a series of experiments, the author has come to the conclusion that the first action of the iodine solution is to add iodine monochloride directly on to the unsaturated bonds in the substance under examination. If in the iodochloride thus formed a carbon atom, to which the iodine or chlorine is attached, be joined also to a negative radical such as $.C_6H_5$ or .COOH, the iodochloride is not very stable. By the action of water it is decomposed, and the iodine or chlorine is replaced by hydroxyl, acid being at the same time produced. The acid may be estimated immediately after the determination of the iodine absorption by adding potassium iodate, and again titrating with thiosulphate. In the case of oils the quantity of hydriodic acid liberated enables one to ascertain approximately the amounts of fatty acid containing one and two unsaturated bonds respectively.

There is a tendency for iodochloride to be decomposed by the action of potassium iodide, the halogen being liberated again. The iodine value may thus appear too low. It is desirable to use sufficient chloroform to retain the whole of the iodochloride in solution, and to add water before introducing the potassium iodide solution. Some of the iodochloride is thus converted into a hydroxyl compound, which is more soluble in the chloroform, and is not so readily decomposed by the potassium iodide.

Waller's solution contains iodine hydrochloride—ICl, HCl—and as this has to be decomposed before addition takes place, it is not only slower in action than Hübl's solution, but also may, on this account, with certain substances yield either no iodine value at all, or one much below the correct amount. This is especially the case where an adjacent negative radical exerts a protecting influence over the unsaturated bonds.

Substitution does not take place during the determination of the iodine value by the methods ordinarily employed. A. M.

Determination of Pentanes and Pentosans. E. Kröber and C. Rimbach; communicated by G. B. Tollens. (*Zeits. f. angew. Chem.*, 1902, xv., 477.)—Compare Analyst, 1899, 178, and 1901, 133. Rimbach has distilled arabinose and xylose with hydrochloric acid of different strengths to ascertain whether the yield of furfurol-phloroglucide is thereby affected. The maximum yield was obtained with acid of specific gravity 1·08 to 1·10, but he recommends that 1·06 be still adhered to, as it is the generally-accepted strength. The distillation is carried out in a metal bath with the constant addition of small quantities of acid, until the distillate no longer gives a red coloration with aniline acetate. More than the calculated quantity of phloroglucinol is dissolved in hydrochloric acid (specific gravity 1·06) and added to the distillate, which is then made up to 400 c.c. and allowed to stand twelve to fourteen hours. The phoroglucide is collected in a porcelain Gooch crucible, using slight suction. It is washed with 150 c.c. of water, taking care to keep the precipitate covered with liquid. It is then dried for four hours in a water-oven, transferred to a stoppered

tube, allowed to cool, and weighed. To the weight found it is necessary to add ·0052 gramme to compensate for phloroglucide dissolved in the acid and wash-water. The corrected weight may be then calculated to furfurol or arabinose, etc. The reaction between furfurol and phloroglucinol takes place in accordance with the equation—

$$C_5H_4O_2 + C_6H_6O_3 = C_{11}H_6O_3 + 2H_2O.$$

More accurate results are obtained by use of Kröber's tables, which are based on a large number of experiments with different pure materials. The following are a few of the figures:

Phloro-glucide.	Fur-furol.	Arabi-nose.	Araban.	Xylose.	Xylan.	Pentose.	Pentosan.
0·030	0·0182	0·0391	0·0344	0·0324	0·0285	0·0385	0·0315
0·050	0·0286	0·0611	0·0538	0·0507	0·0446	0·0559	0·0492
0·074	0·0411	0·0875	0·0770	0·0726	0·0639	0·0801	0·0700
0·100	0·0546	0·1161	0·1022	0·0964	0·0848	0·1063	0·0935
0·169	0·0904	0·1919	0·1688	0·1592	0·1401	0·1756	0·1546
0·200	0·1065	0·2250	0·1984	0·1874	0·1649	0·2065	0·1817
0·300	0·1581	0·3335	0·2935	0·2784	0·2450	0·3060	0·2693

The last two columns are for use in cases where it is not known which pentose or pentosan is present. In most plant substances araban and xylan occur together, but gums contain araban almost exclusively, and wood and straw only xylan.

A. M.

The Initial Action of Iodine and other Oxidizing Agents in the Hydrolysis of Starch and Dextrin. F. E. Hale. (*Zeits. Anorg. Chem.*, xxxi., 100.)—As the result of an elaborate investigation, the author comes to the conclusion that the small loss of iodine, as well as the production of red or purple colorations, which are occasionally met with when arsenious or antimonious oxide is titrated with iodine solution, starch being used as indicator, is probably due to the presence of soluble starch in the starch. A small quantity of this substance appears to be oxidized by the iodine, as well as by hydrogen peroxide or potassium permanganate in alkaline solutions, and the resulting organic acid exerts a hydrolysing action on the remainder with the formation of erythrodextrin, which gives a red colour with iodine. The presence of arsenious or antimonious oxide apparently favours the reaction.

A. G. L.

On Malt Diastase. A. R. Ling and B. F. Davis. (*Journ. Fed. Institut. Brewing*, 1902, viii., 473-495.)—As the result of numerous experiments on the nature of the diastase in different malts used for brewing purposes, the following conclusions are arrived at: Diastase prepared from well-grown, low-dried malt hydrolyses the starch in a 2 to 5 per cent. starch-paste at temperatures between 50° and 60° C. to a point at which the specific rotatory power and the cupric reducing power of the matter in solution, after the hydrolysis has proceeded for about one and a half hours, are:

$$[\alpha]_{D3\cdot93}\ 149\cdot5 - 150. \quad R_{3\cdot93}\ 77 - 78.$$

At the end of twenty-four hours these constants are practically those of maltose, and

in the solution nothing but maltose could be detected. On the other hand, diastase prepared from malt grown under abnormal conditions (*e.g.*, made in the laboratory) does not, even when used in large excess, hydrolyse starch completely to maltose. The nature of the product other than maltose has not yet been determined. A similar effect to the latter is also apparently produced by the action on starch of diastase which has been slowly heated to 115·5° to 120° C.; but diastase which has been rapidly heated to this temperature produces a more pronounced effect. The final temperature at which malt has been kilned is not alone a criterion of its behaviour towards starch, nor is the "diastatic power" as determined by Lintner's method. When diastase is heated in solution to above 65° C. its action on starch paste appears to be quite different to that of diastase solution which has not been heated higher than 60° C. This is indicated by the constants of the matter in solution, and also by the fact that dextrose is invariably present as one of the final products of the hydrolysis. W. P. S.

The Determination of Albuminoid and Proteid Ammonia. L. W. Winkler. (*Zeit. anal. Chem.*, 1902, xli., 290-300.)—According to the author, an estimate of the nitrogenous organic impurities in water can be formed in a much simpler and more certain manner by oxidation with potassium persulphate in acid solution than by the ordinary method of oxidation with alkaline permanganate. Since the amount of ammonia thus split off and determined directly in the liquid without distillation differs from that obtained as albuminoid ammonia, the author distinguishes it by the name of "proteid ammonia." Preliminary experiments with solutions of caffeine and other nitrogenous compounds having shown that there was only a trifling increase in the amount of proteid ammonia after fifteen minutes' heating, that limit of time was adopted in all subsequent determinations. The following table gives the comparative amounts of proteid and albuminoid ammonia obtained from different compounds together with the theoretical quantities:

Substance.	Proteid Ammonia.	Albuminoid Ammonia.	Ammonia Theoretically Obtainable.
	Per Cent.	Per Cent.	Per Cent.
Urea	27·0	2·2	56·67
Hippuric acid	7·4	3·1	9·45
Uric acid	10·6	4·3	40·17
Caffeine	15·2	15·0	26·29
Leucin	10·2	11·3	12·98
Tyrosin	7·9	8·0	10·30
Aspartic acid	11·2	11·8	12·81
Gelatin (18·3 per cent. N.)	9·1	8·2	22·22
Albumin (15·7 per cent. N.)	7·1	6·7	19 06

The solutions required in the determination of proteid ammonia are: (1) Potassium persulphate 1 per cent. solution. In order to free the commercial

salt from ammonium persulphate, 15 grammes are powdered and dissolved in 100 c.c. of water at 60° C., to which is added 1·5 grammes of potassium hydroxide, and the solution filtered through cotton-wool and left for some hours in a cool place. The crystals are collected, washed with cold water, and dried at the ordinary temperature. The solution of the salt is not very stable, but is applicable so long as barium chloride does not produce more than a turbidity. (2) An approximately $\frac{1}{5}$ N. solution of sulphuric acid, prepared by diluting 6 c.c. of pure concentrated acid to a litre. (3) Ammonium chloride solution, containing 0·315 gramme per litre; 1 c.c. = 0·1 milligramme of ammonia. (4) Nessler's reagent, prepared by triturating 10 grammes of mercuric iodide with water, adding 5 grammes of potassium iodide, and mixing the liquid with a completely cold aqueous solution of 20 grammes of sodium hydroxide, the total amount of water used being 100 c.c. Mercuric chloride must not be used for the reagent. (5) Sodium potassium tartrate solution, containing 50 grammes in 100 c.c., with 5 c.c. of Nessler's reagent as a preservative. In the determination of the ammonia equal parts of solutions 4 and 5 are mixed, and termed the "mixed reagent." If any separation of mercuric iodide occur in using this mixed reagent, 0·1 to 0·2 gramme of potassium iodide should be dissolved in 50 c.c. thereof.

In the determination of the proteid ammonia, 100 c.c. of the water under examination are mixed with 5 c.c. of the sulphuric acid solution and 5 c.c. of the potassium persulphate solution, and if the liquid has not then an acid reaction, an additional 5 c.c. of the acid are added. The flask is covered with an inverted beaker and placed on a water-bath in which the water is boiling vigorously, so that the contents of the flask reach a temperature of 90° C. in four to five minutes, and of 95° C. after two or three minutes longer. After fifteen minutes the flask is cooled in a current of water and its contents transferred to a cylinder, into which is also introduced, drop by drop, 5 c.c. of the mixed reagent. At the same time 100 c.c. of the water under examination are placed in a duplicate cylinder and mixed with 5 c.c. (or 10 c.c.) of the sulphuric acid, then with 5 c.c. of the mixed reagent, added drop by drop, and then with 5 c.c. of potassium persulphate solution. The yellow colour of the liquid in the second cylinder will be much fainter than that of the first cylinder. The standard ammonium chloride solution is now added until the colours of the liquids in both cylinders are the same, and the number of c.c. required gives the amount of proteid ammonia in the water.

From the results of experiments on different waters, the author states that in absolutely pure natural water no proteid ammonia is found. He considers that if the proteid ammonia amounts to more than 0·1 milligramme per litre, the water is defective from a hygienic point of view for drinking purposes. Since the method only measures the soluble nitrogenous impurities, the albuminoid ammonia determination is preferable in the case of strongly turbid water and also for coloured waters.

The spontaneous purification of impure water exposed to the air is shown in the following series of determinations. The tap-water before the addition of urine (1 c.c. to 10 litres) contained in 1 litre no free ammonia, 0·05 milligramme of proteid ammonia, no nitrous acid, and 1·6 milligrammes of nitric acid, and required 3·09 milligrammes of potassium permanganate in the oxygen absorption.

Water Containing Urine.	Free Ammonia.	Proteid Ammonia.	N_2O_3.	N_2O_5.	$KMnO_4$ Consumed.
	Milligrammes.	Milligrammes.	Milligrammes.	Milligrammes.	Milligrammes.
Freshly mixed	0·19	0·75	0·00	1·6	5·08
After 1 week	0·20	0·80	0·00	1·7	4·61
,, 2 weeks	0·00	0·77	0·38	2·1	3·91
,, 4 ,, ...	0·00	0·76	0·00	2·7	3·91
,, 6 ,, ...	0·00	0·10	0·00	7·4	3·79
,, 8 ,, ...	0·00	0·09	0·00	10·0	3·06
,, 10 ,, ...	0·00	0·08	0·00	8·5	2·99
,, 12 ,, ...	0·00	0·07	0·00	7·2	2·99

C. A. M.

Examination of Glue and Gelatine. A. Müller. (*Zeits. f. angew. Chem.*, 1902, xv., 482.)—The sample is dissolved in water, and the glutin is precipitated by the addition of a known quantity of tannic acid, the excess of tannic acid being estimated by titration with permanganate. Ten grammes of the sample are allowed to swell in water overnight, then heated and made up to 500 c.c. Quantities of 10 c.c. are taken, and tannin solution (5 grammes in 1 litre) is added gradually, with constant stirring—30 c.c. in the case of leather-glue or gelatine, and 25 c.c. in the case of bone-glue—then 20 c.c. of a 5 per cent. solution of potash alum are added, the liquid is stirred on the water-bath for a minute, then rapidly filtered and washed with water at 30° C. The filtrate is titrated with standard permanganate solution. In order to correct for reducing substances in the glue not precipitated by tannin a second determination is made, in which the filtrate is treated with hide powder and then titrated. The difference between the two gives a measure of the glutin. Under the conditions laid down, 100 grammes of tannin precipitate 139·1 of glutin. The results agree well with those obtained by Kjeldahl's process, but, unlike the latter, they are unaffected by the presence of nitrogenous impurities. A. M.

Estimation of Guanidine. A. Vozárik. (*Zeit. für angew. Chem.*, 1902, xv., 670-672.)—The method is based upon the precipitation of guanidine by picric acid. As the compound formed—$CH_5N_3.OHC_6H_2(NO_2)_3$—is soluble at the ordinary temperature in about 1,280 parts of water, the precipitation is carried out in an ammoniacal solution of ammonium picrate previously saturated with guanidine picrate. This solution is prepared by dissolving 8 grammes of ammonium picrate, 0·075 gramme of guanidine picrate, and 5 c.c. of ammonia (specific gravity 0·91) in 1,000 c.c. of water. In carrying out the process, 8 grammes of the guanidine salt to be tested are dissolved in water which has been rendered ammoniacal, and made up to 1 litre. It is essential that the strength of this solution as regards its guanidine salt contents should be from 0·8 to 1 per cent. After allowing to stand for two to three hours in order that any lead present may settle, 25 c.c. are precipitated by

dropping in 100 c.c. of the ammonium picrate solution. The precipitate is filtered after standing six to twelve hours through a Gooch's crucible containing a little asbestos, washed with ammonium picrate solution (the latter being removed as much as possible by suction), dried at 110° C., and weighed. The precipitate retains about 1 per cent. of its weight of the ammonium picrate solution, and the asbestos 2·5 per cent. of its weight. The weight of the precipitate is corrected for these amounts.

W. P. S.

To Distinguish the different Varieties of Carbon. E. Donath and B. Margosches. (*Chem. Ind.*, 1902, xxv., 226.)—In consequence of the use of different modifications of carbon for the manufacture of arc-light pencils and electrodes, it is of importance to be able to distinguish them. One is able to do this to some extent by taking advantage of their different behaviour to oxidizing agents. Diamonds are not attacked by a mixture of potassium chlorate and concentrated nitric acid. They burn in oxygen to carbon dioxide at temperatures above 700°. They are rapidly attacked by fused alkaline carbonates.

Graphite, on treatment with fuming nitric acid and potassium chlorate, is oxidized to graphitic acid. Some varieties of natural graphite, when soaked in a little nitric acid and then ignited, swell up with the formation of worm-like excrescences. Those varieties that do not give this reaction have been termed "graphitite" by Luzi. Graphite is not attacked by nitric acid (1·4), and only slowly by a mixture of this with concentrated sulphuric acid.

Graphite, retort carbon, coke, and petroleum coke are not dissolved by boiling nitric acid (1·4), but are attacked somewhat by a mixture of this with concentrated sulphuric acid. Anthracite, coal, brown coal, charcoal, sugar charcoal, soot, and pure amorphous carbon are partially dissolved by the nitric acid with the formation of an intense brownish-red coloration. In the mixture of nitric and sulphuric acids solution is more rapid.

By boiling with concentrated alkaline permanganate solution coal and brown coal are oxidized to oxalic acid. Graphite, on the other hand, is not attacked, and coke and charcoal only to a small extent. Brown coal, lignite, and pitch may be distinguished from coal by treating with brominated potash. The former dissolves readily, but the latter is little affected. Charcoal also is but little attacked.

Graphite and coke can be differentiated by fusion with sodium sulphate. The former is unaffected, but the latter reduces the sulphate to sulphide and sulphite.

A characteristic property of charcoal is that, on continued heating with concentrated sulphuric acid, it dissolves with the formation of sulphurous acid and brown coloration. Coal under the same conditions is not entirely dissolved.

Ordinary soot and lamp-black may be distinguished from soot made from naphthalene by extracting with petroleum ether. The latter yields a fluorescent solution, which on evaporation leaves a residue of characteristic odour.

Valuable information may often be obtained by submitting a sample to dry distillation, or by examining for impurities, such as nitrogen and sulphur. Microscopic examination, combined with treatment with chromic acid, is also often useful.

The amount of anthracite in an adulterated graphite may be roughly estimated

by observing the coloration produced on boiling with nitric acid, and the quantity of oxalic acid produced by treatment with alkaline permanganate. Charcoal may be detected in the presence of coke by the coloration with nitric acid. Retort carbon is distinguished from graphite by not giving Brodie's graphitic acid reaction. Electric graphite can be distinguished from natural only by its physical properties. A. M.

INORGANIC ANALYSIS.

The Determination of Copper as Cuprous Thiocyanate in the Presence of Bismuth, Antimony, Tin, and Arsenic. R. G. van Name. (*Zeits. Anorg. Chem.*, xxxi., 92.)—The author finds that the separation of copper from bismuth by precipitation as thiocyanate is not very satisfactory, even in the presence of both hydrochloric and tartaric acids, as the presence of much free acid exerts a solvent action on the precipitate, whilst if too little acid is present the latter will be contaminated with basic salts of bismuth. He finds it best to start with a fairly acid solution of the two metals, and roughly ascertain, by means of a few blank tests on separate portions of the solution, the maximum quantity of ammonium bisulphite solution which may be added (to neutralize the acid) without precipitating bismuth. From antimony and tin, on the other hand, the separation is easily effected in the presence of small quantities only of hydrochloric and tartaric acids, whilst for the separation from arsenic the presence of a fair amount of hydrochloric acid is all that is necessary. A. G. L.

On a Modification of Rose's Method of Separating Nickel and Cobalt. R. L. Taylor. (*Chem. News*, lxxxv., 269.)—In Rose's method the cobalt is precipitated as sesquioxide from dilute solutions containing free hydrochloric acid by means of bromine or chlorine, and barium, strontium or calcium carbonate, nickel remaining in solution. The process, even as modified by Henry (*Chem. Gazz.*, 1855, 237), requires several hours, and has consequently fallen into disuse. The author of the present paper found, however, that if neutral solutions are used instead of acid ones, the method not only becomes more accurate, but the precipitation of the cobalt is complete in a few minutes. From his experiments, he comes to the conclusion that the retarding effect of the free acid on the precipitation of cobalt is due to the production of considerable quantities of free carbonic acid. The method, as recommended by him for both quantitative and qualitative analysis, consists simply in adding to the cold neutral solution of the metallic chlorides a paste of precipitated barium carbonate and water and then bromine water, allowing to stand for ten minutes, and filtering the precipitate off. If the solution is allowed to stand for more than an hour in contact with air some nickel may be precipitated. If the solution of the chlorides contains free acid, this must be removed by evaporation, neutralizing with a caustic alkali, or else by adding excess of barium carbonate, boiling to expel the free carbonic acid, and cooling before adding the bromine water.

A. G. L.

The Volumetric Determination of the Double Phosphates of Ammonium with Cadmium, Cobalt, Manganese, and Zinc. H. D. Dakin. (*Zeit. anal. Chem.*, 1902, xli., 279-284.)—The method consists of dissolving the precipitate of the double phosphate in an excess of normal acid, and titrating the excess with normal alkali, using methyl orange as indicator, as in Stolba's method of titrating ammonium magnesium phosphate. The end-point of the titration is reached when the metal present is converted into sulphate or chloride and the phosphoric acid into mono-phosphate. Thus :

$$M^{II}(NH_4)PO_4 + H_2SO_4 = M^{II}SO_4 + (NH_4)H_2PO_4.$$

Cadmium ammonium phosphate precipitated in the cold and dried at 100° C. contains 1 molecule of combined water. In test experiments the amounts of cadmium found were within 0·0007 gramme of the theoretical amounts. The conditions for the quantitative separation of cobalt, manganese, and zinc as double phosphates with ammonium were described in a former communication (*Zeit. anal. Chem.*, xxxix., 273 and 784). In each case satisfactory results were obtained in the test experiments. (*Cf.* Walker, ANALYST, xxvi., 304.) C. A. M.

The Detection of Traces of Vanadium, and the Separation of Vanadium from Molybdenum. P. Truchot. (*Ann. de Chim. anal.*, 1902, vii., 167, 168.)—In the author's electrolytic method of determining vanadium, the deposit on the cathode is brownish-yellow and more or less iridescent. On washing the deposit with water and alcohol, evaporating the latter by gentle heat, and treating the deposit with a little potassium bisulphate and 2 to 3 drops of sulphuric acid, a characteristic yellow coloration is obtained.

On now adding a few crystals of strychnine sulphate, a bluish-violet colour changing to rose is produced.

This reaction is capable of detecting 1 part of vanadic acid in 100,000.

The colorations given by other alkaloids and by phenols with vanadic anhydride are as follows : Atropine, nil ; caffeine, nil ; santonin, nil ; phenol, dark green ; and pyrogallol, very dark brown.

Separation of Vanadium from Molybdenum.—Molybdenum is deposited as a black hydroxide upon the cathode under exactly the same conditions as described above in the case of vanadium. On ignition, this hydroxide is converted into molybdic acid, which is completely volatilized at a red heat.

When both vanadium and molybdenum are present, the deposit is first ignited gently and then strongly until the weight becomes constant.

As a rule, the ignition is complete in about thirty minutes when the mixture of the two oxides is not more than 0·1 gramme. C. A. M.

The Determination of Vanadium. H. Cormimbœuf. (*Ann. de Chim. anal.*, 1902, vii., 258-260.)—The following simple modification of Roscoe's method is stated to be more accurate than other gravimetric methods, and to take only twenty-four hours : The vanadium compound is converted into potassium or sodium vanadate,

which is dissolved in water, and filtered from the insoluble oxides of iron, magnesium etc. The filtrate is acidified with acetic acid and a sufficient quantity of lead acetate added. Under these conditions the vanadic acid is completely precipitated, although the lead vanadate is not always constant in composition. The precipitate is collected on a weighed filter, washed with water containing a little acetic acid, dried at 100° C. and weighed. It is then detached from the paper and pulverized in a mortar. A weighed portion of the powder is dissolved in water acidulated with nitric acid, and the lead precipitated by adding a slight excess of concentrated sulphuric acid. The liquid is slightly diluted with water and filtered from the lead sulphate, and the filtrate evaporated to dryness in a weighed porcelain crucible on the water-bath. The temperature is then gradually raised until, finally, it reaches red heat, at which stage the vanadic acid is partially fused and quite pure. The crucible is then cooled and weighed, and the total amount of vanadic acid in the lead vanadate calculated from the weight thus obtained from the aliquot portion. C. A. M.

The Determination of Thallium in the Thallous State. V. Thomas. (*Bull. Soc. Chim.*, 1902, xxvii., 470-471.)—The author's method is based upon the oxidation of the thallous salt by means of gold bromide, and the gravimetric determination of the metallic gold—

$$3TlCl + 2AuBr_3 = 3TlClBr_2 + 2Au.$$

About 5 grammes of the salt (chloride) are dissolved in hot water, and the solution heated on the water-bath and treated with a solution of gold bromide in sufficient quantity. The whole is then kept hot for eight or ten hours, after which the gold is collected on a filter, dried, and weighed. The weight of gold multiplied by the factor, 1·5533, gives the weight of thallium. In this way the author obtained five results ranging from 85·02 to 85·30 per cent. of thallium, the theoretical amount in thallous chloride being 85·21 per cent. The gold bromide solution is prepared by dissolving gold in hydrobromic acid containing bromine, and evaporating the solution to dryness on the water-bath. The crystals (bromo-auric acid) are dissolved in water, and the solution filtered before use if necessary. C. A. M.

The Separation of Beryllium. G. Wyrouboff. (*Bull. Soc. Chim.*, 1902, xxvii., 733, 734.)—There is considerable difficulty in effecting a quantitative separation of beryllium from iron and aluminium, with which it is invariably associated in the emerald. In examining various compounds of beryllium, the author has found that the oxalate, $Be_2O_3(C_2O_3)_6.3K_2O$, is only sparingly soluble, 100 parts of water dissolving 1·4 parts of the salt at 15° C., whilst the corresponding oxalates of iron, aluminium, and chromium are soluble in two or three times their weight of water. In this way it is possible to effect a rapid and approximately complete separation of beryllium. The mineral is attacked with potassium hydroxide, the silica removed in the usual way, and the solution of chlorides evaporated to a small volume and treated with a concentrated solution of potassium hydrogen oxalate. The crystalline precipitate, which is soon deposited, is washed with water, and is quite free from iron or aluminium. C. A. M.

A Colour Reaction of Uranium Salts and Hydrogen Peroxide. J. Aloy. (*Bull. Soc. Chim.*, 1902, xxvii., 734, 735.)—On treating a salt of uranium with hydrogen peroxide and then with potassium carbonate in either the solid form, or in a concentrated solution, a red coloration is produced, and on then adding to the liquid two or three times its volume of alcohol a red precipitate is rapidly deposited. In applying this test to the detection of traces of hydrogen peroxide, it is best to make a solution of uranium nitrate in 95 per cent. alcohol, then to add a few drops of the liquid under examination, and, lastly, a few crystals of potassium carbonate. The reaction takes place in two stages, a white peruranic hydroxide being formed by the action of the hydrogen peroxide, and subsequently decomposed by the alkali carbonate. The red precipitate is very unstable, rapidly losing part of its oxygen at the ordinary temperature. C. A. M.

Aromatic Bases as Precipitants for Rare Earth Metals. Alice MacMichael Jefferson. (*Journ. Amer. Chem. Soc.*, xxiv., 540.)—The behaviour of six of the rare earth metals with aromatic bases was examined, and it was found that zirconium is precipitated quantitatively in the form of double salts by aniline, o-toluidine, xylidine, dimethyl- and diethyl-aniline, benzylamine, pyridine, piperidine, and quinoline. Thorium is precipitated by aniline, o-toluidine, xylidine, dimethyl-aniline, diethyl-aniline, pyridine, piperidine, and quinoline. Cerium is completely precipitated by aniline, o-toluidine, diethyl-aniline, benzylamine, pyridine, and piperidine, whilst lanthanum, neodymium, and praseodymium are only precipitated by benzylamine and piperidine.

Fairly good separations can consequently be effected by quinoline of thorium and zirconium from neodymium, and by aniline of thorium and zirconium from lanthanum; lanthanum and thorium may also be separated by means of quinoline. O-toluidine separates cerium from praseodymium; thorium and praseodymium may be separated by aniline, and lanthanum and praseodymium from thorium by means of xylidine. In most cases it is advantageous to repeat the separations.

A. G. L.

Analyses required for an Electrolytic Alkali Works. J. H. James and J. C. Ritchey. (*Journ. Amer. Chem. Soc.*, xxiv., 469.)—The free chlorine, sodium hypochlorite, and sodium chlorate in the spent brine are determined as follows: For free chlorine, 50 c.c. of the brine are treated with 10 c.c. of a saturated solution of potassium iodide for five minutes, and the liberated iodine titrated with decinormal thiosulphate solution. For sodium hypochlorite, 50 c.c. of the brine are titrated with arsenious acid, using drops of starch and potassium iodide solution on a plate as indicator. The hypochlorite is obtained by subtracting from the value found the equivalent of the chlorine found above. For sodium chlorate, 50 c.c. are placed in an 8-ounce flask, the quantity of arsenious acid solution found above to be equivalent to the free chlorine plus sodium hypochlorite is added, and then a weighed amount of ammonium ferrous sulphate in excess of the chlorate present. The flask is closed by a small funnel, heated, and 15 c.c. concentrated sulphuric acid are slowly added,

1 c.c. at a time, after which the solution is boiled gently for three or four minutes. After cooling, the excess of ferrous salt is titrated with bichromate solution. The quantity of ferrous salt oxidized corresponds to the chlorate present.

The quantity of water in the bleaching powder is determined by heating a mixture of 1 gramme of the sample with 5 grammes of copper oxide in a porcelain boat placed in a porcelain tube. The water driven off is absorbed in a sulphuric acid tube and weighed. Between the boat and the absorption tube a mixture of scrap sheet and cement silver is placed to absorb any chlorine escaping from the boat. The tube is heated gently at first, the portion under the boat being finally raised to the hottest temperature obtainable, and kept at this temperature for one hour and a half. A current of dry air is drawn through the tube during the heating. The reaction in the boat occurs according to the equation :

$$Ca(OCl)_2 + 4CuO = CaCl_2 + 2O_2 + 2Cu_2O.$$

A. G. L.

The Microchemical Detection of Alkalies and Acids. F. Emich. (*Monatsh. für Chem.*, 1901, xxii., 670-678; and 1902, xxiii., 76-80.)—*Microchemical Detection of Acids and Alkalies by means of "Litmus Silk."*—Silk dyed with a purified solution of litmus is recommended as a suitable reagent. The red silk is prepared by boiling the silk with a solution prepared by extracting commercial litmus with water, rejecting the first extract, boiling the residue with a fresh portion of water, filtering the solution, and adding sulphuric acid in excess to the boiling filtrate. After thirty minutes the dyed silk, which has a violet-red colour, is washed in a current of water, dried, and kept in the dark.

The blue silk is prepared by soaking the red silk in water rendered faintly alkaline, washing it rapidly, pressing it between filter-paper, and drying.

In using the litmus silk, a single cocoon fibre is fixed to a fragment of wax and cut with sharp scissors so as to leave about a centimetre free. This is purified with a drop of alcohol, and examined under the microscope to insure absence of impurities. A droplet (about 0·05 milligramme) of the liquid is then placed on a suitable surface, and the end of the silk introduced, and after the evaporation of the liquid again examined under the microscope.

The smallest quantities of an alkali or acid are capable of detection by this method. C. A. M.

Common Errors in the Determination of Silica. W. F. Hillebrand. (*Journ. Amer. Chem. Soc.*, xxiv., 362.)—The author calls attention to the known fact that at least two evaporations, alternating with two filtrations, are absolutely necessary in order to render silica insoluble. He also shows that the generally accepted view that the silica in the filtrate is completely precipitated by ammonia or sodium acetate, if sufficient iron or aluminium is present, is incorrect, and that the silica contained in the oxides of iron and aluminium is only partly left undissolved when the oxides are fused with potassium pyrosulphate and the melt treated with water or acid, since silica is appreciably soluble in fused potassium pyrosulphate. The statement of

Lunge and Millberg (*Zeits. angew. Chem.*, 1897, 425), that silica can be rendered completely anhydrous merely by ignition over a Bunsen burner, is found by the author to be correct as regards the silica obtained by the action of water on silicon tetrafluoride, but does not apply to silica separated by acids from silicates, for which the prolonged use of the blow-pipe is necessary. A. G. L.

A New Volumetric Method for the Determination of Free and Combined Sulphuric Acid. W. Müller. (*Berichte*, 1902, xxxv., 1587-89.)—This is based upon the fact that sulphuric acid is precipitated by benzidene hydrochloride. The solubility of benzinide sulphate, according to the author's experiments, at 25° C. is about 0·02 per cent., and this is diminished both by the addition of sulphuric acid and of benzidene salts. It is, moreover, possible, on the other hand, to titrate the combined acid in a benzidene salt with standard alkali, phenolphthalein being used as indicator, and thus to standardize the benzidene hydrochloride solution.

By using a measured excess of benzidene hydrochloride and determining the amount left in the filtrate from the precipitate, the difference corresponds with the amount of sulphuric acid. Since benzidene sulphate mechanically carries down a little benzidene hydrochloride from a cold solution, the precipitation should be made from a hot solution. A definite quantity of the sample under examination is titrated with alkali, using phenolphthalein as indicator, and the neutralized solution diluted to 150 c.c. and warmed on the water-bath. A measured excess of 20 to 30 per cent. of benzidene solution beyond the amount required to effect complete precipitation is then added, and the flask kept on the water-bath for a few minutes until the benzidene sulphate separates. The liquid is then cooled, diluted to 250 c.c., and filtered, and an aliquot portion of the filtrate titrated back with standard alkali. The difference between the amount of alkali required by the benzidene hydrochloride used and that now consumed gives the amount of sulphuric acid. C. A. M.

The Detection of Nitric Acid in the Presence of an Alkali-metal Ferrocyanide or Ferricyanide. A. F. Leuba. (*Ann. de Chim. anal.*, 1902, vii., 258.)—The test for nitric acid by the addition of sulphuric acid and a ferrous salt to the solution cannot be made in the usual manner in the presence of alkali-metal ferrocyanides or ferricyanides, since these form dark-blue compounds. To obviate this, a slight excess of a concentrated solution of cadmium chloride is added, the liquid filtered from the insoluble cadmium ferro- or ferri-cyanide, and the test for nitric acid applied to the filtrate. C. A. M.

On the Influence of Potassium Ferrocyanide on the Precipitation of Phosphoric Acid. A. F. Leuba. (*Ann. de Chim. anal.*, 1902, vii., 257.)—Potassium ferrocyanide interferes with the precipitation of phosphoric acid by ammonium molybdate, owing to its yielding a dense reddish-brown precipitate, to which has been assigned the formula $Mo(OH)_4$. This precipitate is soluble in an excess of hot

nitric acid, forming a brown solution, from which, however, the phospho-molybdate still does not separate. On the other hand, the brown precipitate readily dissolves in sodium carbonate solution, and on exactly neutralizing the liquid with nitric acid and heating it very slightly the yellow phospho-molybdic compound separates out.

C. A. M.

Iodometric Determination of Ferro- and Ferri-cyanides. E. Rupp and A. Schiedt. (*Berichte*, vol. xxxv., p. 2430.)—In De Haen's method for the titration of ferrocyanides with permanganate the end-point is indistinct, and the results are, as a rule, from 1 to 3 per cent. too high. Contrary to the statement in the text-books that ferrocyanides cannot be quantitatively oxidized with iodine, the authors show that satisfactory results can be obtained by using an excess of iodine solution and titrating back with thiosulphate. In presence of organic matter (tartrates) the oxidation is not complete. Ferricyanides are reduced by boiling in strongly alkaline solution with ferrous sulphate, and in an aliquot portion of the filtrate, the ferrocyanide produced is titrated. O. H.

Old and New Reactions of Ozone. C. Arnold and C. Mentzel. (*Berichte* 1902, xxxv., 1324-1330.) — Zinc iodide starch solution, potassium iodide starch solution, and guaiacum tincture are not characteristic reagents for ozone, since they also become blue on contact with chlorine, bromine, or nitric oxide.

Houzeau's test, too, which is based upon the blue coloration of red litmus-paper, dipped in potassium iodide solution, is quite unreliable, for the authors found that all the commercial test-papers examined by them became blue on contact with a dilute solution of iodine. They therefore made experiments to determine the value of other indicators as reagents, and found that only phenolphthalein, rosolic acid, and fluorescein were applicable.

Paper saturated with a mixture of a 15 per cent. solution of potassium iodide and with a sufficient quantity of a 1 per cent. alcoholic solution of phenolphthalein to render the liquid opalescent, was coloured a fugitive red by ozone, whilst chlorine, bromine, or nitric oxide only gave blue or brown colorations. In like manner paper moistened with a mixture in equal parts of a 15 per cent. solution of potassium iodide, and a 1 per cent. alcoholic solution of rosolic acid became bright red on contact with ozone. The fluorescein test-paper was prepared by moistening black paper with a 1 per cent. solution of potassium iodide and a solution of fluorescein. It gave a green fluorescence in the presence of ozone.

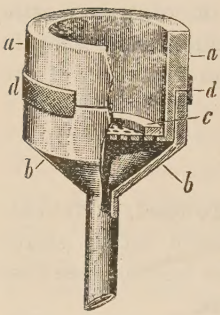
Erlwein and Weyl's phenylenediamine test did not prove satisfactory in the authors' hands, though they found paper moistened with a mixture of paraphenylediamine and potassium acetate solutions to give characteristic reactions, yielding on contact with ozone a green colour changing to brown, and a blue or violet colour with chlorine, bromine, or nitric oxide.

Benzidene was found to be a very distinctive reagent. Test-paper prepared by moistening paper with a saturated alcoholic solution of that substance gave a brown

coloration with ozone, whilst nitric oxide and bromine produced a blue coloration, and chlorine a blue colour changing to reddish-brown. Hydrogen peroxide was without action upon the benzidene test-paper, but a mixture of benzidene and copper sulphate solutions gave a blue precipitate with traces of hydrogen peroxide.

A still more sensitive and characteristic reagent for ozone was discovered in tetramethyl-*p*-*p*'-diamido-diphenylmethane. Test-paper soaked in an alcoholic solution of that compound became violet in the presence of ozone, deep blue with chlorine or bromine vapour, and faint yellow with nitric oxide, whilst it remained colourless on contact with hydrogen peroxide. C. A. M.

APPARATUS.



An Improved Büchner's Funnel. J. Katz. (*Chem. Zeit.*, 1902, xxvi., 356.)—As will be seen from the accompanying diagram, this apparatus is specially suitable for quantitative filtrations with the pump, as the space under the plate is accessible for cleaning purposes. *d* is a rubber ring sprung round the joint; thus the whole is made airtight without any danger of contaminating the solution with indiarubber. *c* is a porcelain ring which lies on the edge of the paper, and prevents it from being displaced. The funnel is made by F. Hugershoff of Leipzig. F. H. L.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

The next final Examination for the Associateship in the Branch of Biological Chemistry will be held at the Institute on Tuesday, the 21st day of October, 1902, and three following days.

The Examination is open to any Candidate whose application for admission to the Final Examination has been accepted by the Council, and to any Candidate who has passed the Intermediate Examination of the Institute.

The Examination will extend over four days, and may be theoretical, practical, written, and oral, and the syllabus will include the following:

BIOLOGICAL CHEMISTRY, with special reference to the Chemistry and Bacteriology of Foods, Water, Sewage, and Effluents, and the practical applications of Biological Chemistry to Industries.

Candidates presenting themselves in any Branch of the Final Examination are expected to possess a general knowledge of all branches of Chemistry in addition to a *thorough* knowledge of the particular Branch of Chemistry selected.

ERRATUM.

In this volume, page 236, fifth line from bottom, *for* "Victoria" *read* "Nelson.